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CaF_2 Laser Crystal Growth,
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(10) by
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Director, ARPA:

The preparation of crystals of CdF_2 doped with various rare earth and transition ions has continued. The concentration of impurities (other than those deliberately added) seems to be less than 1 ppm and the band edge in the pure crystals is about 6.1 ev (2050A). We now have grown crystals containing each of the rare earth ions (about 0.1%) except Pm, Ce, and Tb. The oxidation state in all cases is +3 and the absorption spectra have been measured at room temperature and at 77°K. The spectra are quite similar to those previously measured for the host CaF_2; the peak absorptions having only slightly different wavelengths in the two cases. The fluorescence spectrum of $CdF_2:Nd^{+3}$ in the neighborhood of 1μ indicates that the crystal field splitting is slightly smaller in CdF_2 than in CaF_2. The fluorescence spectra of the other rare earth ions in CdF_2 have not yet been measured.

The emission of CaF_2:Cr has been measured at 77°K and is a single broad (1000A wide) band whose maximum at 7150A corresponds closely to that of the lowest energy band seen in absorption. This observation seems to confirm the previously given interpretation that the impurity is Cr^{+3} at a Ca site and the crystal field strength is about 1400 cm^{-1}. The excited state is a mixture of $^4T_2$ ($e^2t_2^2$) and $^2T_1$, $^2T_2$ (e^2t_2), whereas the ground state is a mixture of $^4T_1$ (e^2t_2) and ^2E (e^3). The detailed nature of these states and a more accurate interpretation is in progress. The secular equations for the d^3 system in the hexahedral symmetry will be solved for a range of parameters on electronic calculators.

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The absorption spectrum of a sample of CdF_2 containing 5% MnF_2 has been observed. The bands are very weak and lie at 17,000, 22,000, 24,100, and 25,300 cm^{-1}. The sample seems to emit feebly in the green, but has not yet been subjected to a spectral analysis. Qualitatively, the absorption spectrum is similar to that previously observed in ZnS, but the bands are shifted to higher energies in CdF_2. Samples containing higher concentrations of Mn will be grown in order to check the dependence of band intensity on concentration. This should show if pairs (and higher clusters) of Mn ions occur and have a large interaction as they do in ZnS; (see D. S. McClure, J. Chem. Phys. 39, 2850 (1963).

One attempt to reduce a +3 rare earth ion to the +2 state in CdF_2 by γ - irradiation failed. The same ion, Ho^{+3}, in CaF_2 can be reduced in this way, however we do not know if the method will work for CdF_2. Attempts to reduce ions in this host by heating in the presence of Cd vapor are in progress.

The 2 meter B and L grating spectrograph has been received, aligned, and checked. We shall be doing some of the higher resolution and emission studies on this instrument.

The Fabry-Perot interferometer has been improved with the addition of a new camera; a new fine focus adjustment is near completion. A 50 inch long 6328A He-Ne gas laser has been used to line up and calibrate the interferometer. With a 13 cm interferometer plate spacing, the maximum now available, six longitudinal modes of the laser was clearly resolved with an observed separation of 120±4 Mc, while that calculated from the laser length is 118±1 Mc. The longitudinal modes were first resolved with a plate spacing of 7 cm; the observed finesse of the present silvered surfaces was 25±5. These figures give a resolution at the 13 cm spacing of 50±15 Mc (at 6328A) or about 0.002 cm^{-1}.

Further attempts to measure the line width and hyperfine splitting of the Tm^{+2}:CaF_2 1.116μ fluorescence with this instrument have not yet confirmed the preliminary data quoted in the last report. These efforts will continue after good alignment of the instrument using the nearby 1.15μ gas laser line has been achieved. Alignment at these wavelengths is considerably more difficult than for the visible 6328A line, and the data are not yet very good.

Another technique is being investigated for high resolution studies of the sharp 4f-4f transitions at 2.36μ in the CaF_2:Dy^{+2} system. The method is

equally applicable to the 1.16μ line of the $CaF_2:Tm^{+2}$ system. These experiments involve the resonance absorption of the fluorescent radiation by an absorber crystal in a homogenous magnetic field, H. If both the fluorescent and absorbing crystals are at the same temperature, the resonance absorption is a maximum for H=0. As H increases, the absorbing line is Zeeman split and has an accurately known g-value and the absorption of the undeviated fluorescent line is reduced. If the two crystals are of different temperatures, then the H=0 absorption may be small and increase as various Zeeman components are tuned through the fluorescent line with increasing H.

Experiments to date show energy shifts of 0.22 cm^{-1} for the $^5I_7\ T_1^{(2)}$ to $^5I_8\ T_2^{(2)}$ (laser) transition and 0.33 cm^{-1} for the $^5I_7\ T_1^{(2)}$ to $^5I_8$ E (ground state) transition as the temperature is reduced from 77°K to 27°K. For the orientation used, light incident || [100] and H $\perp$ [100], the g=10 (relative) components are not observed. Second order splittings of some components have not been observed but should become resolved at lower temperatures. Precise line width determinations have not yet been made.

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